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Feature article

A review of stimuli-responsive shape memory polymer composites

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ABSTRACT

The past decade has witnessed remarkable advances in stimuli-responsive shape memory polymers (SMPs) with potential applications in biomedical devices, aerospace, textiles, civil engineering, bionics engineering, energy, electronic engineering, and household products. Shape memory polymer composites (SMPCs) have further enhanced and broadened the applications of shape memory polymers. In addition to reinforcement, SMPCs can enable or enhance athermal stimuli-active effects, novel shape memory effect, and new functions. Many athermal stimuli-responsive effects have been achieved such as electroactive effect, magnetic-active effect, water-active effect, and photoactive effect. The typical examples of novel shape memory effects are multiple-shape memory effect, spatially controlled shape memory effect, and two-way shape memory effect. In addition, new functions of SMPCs have been observed and systemically studied such as stimuli-memory effect and self-healing. This feature article presents an up-to-date review on these versatile SMPCs. The various methods to fabricate these SMPCs and the performances of the SMPCs are discussed. The potential directions for future advancement in this field are also discussed.

1. Introduction

Stimuli-responsive polymers significantly change their properties such as shape, mechanical properties, phase separation, surface, permeability, optical properties, and electrical properties upon small variation of environmental conditions such as temperature, electric field, pH, light, magnetic field, electrical field, sonic field, solvent, ions, enzymes, and glucose [1–7]. Since 2010, three special and themed issues have been devoted to these smart materials: “Stimuli-responsive materials” in Progress in Polymer Science (2010, Vol. 35, issue 1-2); “Stimuli-sensitive polymers” in Advanced Materials (2010, Vol. 22, issue 31); and “Actively moving polymers” in Journal of Materials Chemistry (2010, Vol. 20, issue 17).

Shape memory polymers (SMPs) as a type of important stimuli-responsive polymers, can recover their original (or permanent) shape upon exposure to external stimuli [8–14]. Many review papers have been published on various SMPs especially thermal-responsive SMPs [15–35]. Since the report of the first SMP, shape memory polynorbornene (high macromolecular weight with abundant physical cross-linking), numerous SMPs based on different structures have been developed in labs and several typical ones have been commercialized in large scales such as polyurethane (DiAPLEX, SMP Technologies Inc., originally from Mitsubishi Heavy Industries), polystyrene based SMP (Veriflex®, Verilyte™, Veritex™, Cornerstone Research Group, Inc.), aliphatic polyurethane (Tecoflex®, Lubrizol Advanced Materials), epoxy based SMP (TEMBO®, Composite Technology Development, Inc.), and UV curable polyurethane (NOA-63, Norland Products Inc.).

A stable polymer network and a reversible switching transition of the polymer are the two pre-requites for the shape memory effect (SME) (see Fig. 1). The stable network of SMPs determines the original shape, which can be formed by molecule entanglement, crystalline phase, chemical cross-linking, or interpenetrated network [36–42]. The lock in the network represents the reversible switching transition responsible for fixing the temporary shape, which can be crystallization/melting transition [38,40,43–45], vitrification/glass transition [25,35,38,43–82], liquid crystal anisotropic/isotropic transition [83–89], reversible molecule

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Abbreviations: CB, carbon black; CD, cyclodextrin; CNF, carbon nanofiber; CNP, carbon nanopaper; CNT, carbon nanotube; IPN, interpenetrating polymer network; MSME, multiple-shape memory effect; MSMP, multiple-shape memory polymer; MWCNT, multi-walled carbon nanotube; PCLDMA, poly(caprolactone) dimethacrylate; PEGMA, poly(ethylene glycol)mono-methylether-monomethacrylate; SMA, shape memory alloy; SME, shape memory effect; SMP, shape memory polymer; SMPC, shape memory polymer composite.

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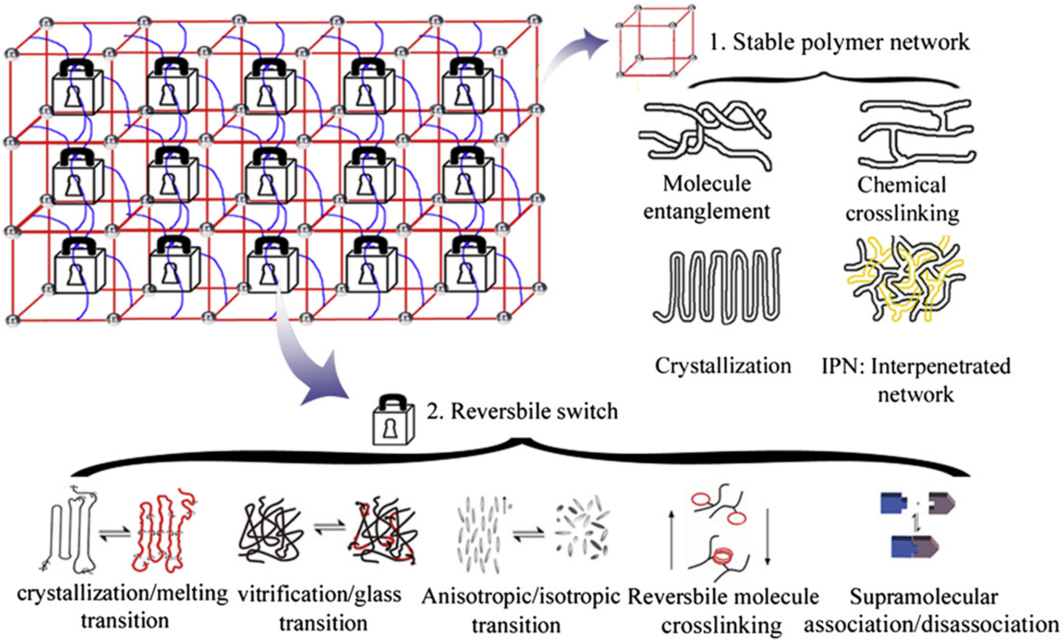

Fig. 1. Various molecular structures of SMPs. A stable network and a reversible switching transition are the prerequisites for the SMPs to show SME. The stable network can be molecule entanglement, chemical cross-linking, crystallization, and IPN; the reversible switching transition can be crystallization–melting transition, vitrification–glass transition, anisotropic–isotropic transition, reversible chemical cross-linking, and association–disassociation of supramolecular structures.

cross-linking, and supramolecular association/disassociation. Typical reversible molecule cross-linking reactions as switching transitions include photodimerization [8,90–94], Diels–Alder reaction [95–103], and oxidation/redox reaction of mercapto group [104]. Typical switching transition per supramolecular association/disassociation includes hydrogen bonding [105–113], self-assembly metal–ligand coordination [114,115], and self-assembly of β-CD [116–121]. In addition to the above reversible switches, other stimuli which can significantly change the mobility of the SMP may also trigger the SME, such as moisture, water/solvent, ions, pressure, light, pH, etc. [24].

SMPs can be used widely in many areas such as biomedical devices, aerospace, textiles, energy, bionics engineering, electronic engineering, civil engineering, and household products. It is difficult to extensively elaborate all the applications. Table 1 summarizes the typical applications of SMPs. For detailed application strategies, reader could go to the specified references.

The first research of shape memory polymer composites (SMPCs) may be reinforcement of SMPs. SMPs have intrinsic low mechanical strength and shape recovery stress, which have largely restricted the applications of SMPs. A small amount of reinforcing fillers is able to improve the mechanical performance and shape recovery stress of SMPs. In addition to reinforcement effect, SMPCs can enable or enhance athermal stimuli-active effects, novel SME, and new functions as shown in Fig. 2. The examples of athermal stimuli-responsive effects include electroactive effect, magnetic-active effect, water-active effect, and photoactive effect. The novel SMEs include multiple-shape memory effect, spatially controlled SME, and two-way SME. The two examples of new functions are stimuli-memory effect such as magnetic field-memory effect, and self-healing effect of SMPCs such as thermoplastic particles filled SMPs.

This paper is intended to present a comprehensive review of the recent progress of these various SMPCs in terms of the reinforcement, athermal stimuli-responsive effect, novel SME, and the new functions. The various methods and recent progress to fabricate these SMPCs are presented. Though researchers are now able to design various SMPCs with different properties for various applications, there are still many challenges to overcome. The research challenges in this field are discussed and future research needs are identified. By comprehensively summarizing the research in this area, we hope this paper can not only help interdisciplinary readers to understand the state-of-the-art in this area but also shed some light on future research directions in this research field.

2. Reinforcement of shape memory polymers (SMPs)

Although outstanding in many aspects as compared with SMAs, SMPs have intrinsic low mechanical strength and shape recovery stress. These problems have largely restricted the applications of SMPs. Reinforcing fillers are able to improve the mechanical performance and shape recovery stress of SMPs through physical blending, in-situ polymerization and chemical cross-linking [15,48,180,182,283–290].

2.1. *Reinforcement by microfibers, fabrics, and mats*

Microfiber, fabrics and mats made of carbon fibers, glass fibers and Kevlar fibers have high elastic modulus and high strength, and can remarkably increase the mechanical strength of SMPs [291]. These composites, in the fiber (axial) direction, can bear much higher mechanical load; while in the transverse direction, the SME can be mostly maintained [292]. These reinforced SMPCs are mostly proposed to be used for spacecraft self-deployable structures [190,292–295] and vibration control structures [296–301]. Few updated research was reported in the last five years on these SMPCs, which may be partially because the microfiber, fabric and mat can lower the SME of the SMP matrix, especially in the reinforcement direction.

2.2. *Reinforcement by carbon nanotubes (CNTs) or carbon nanofibers (CNFs)*

One of the main objectives of incorporating CNTs or CNFs into SMP is to achieve electroactive SME by Joule heating in intrinsic